

THE ABSORPTIVE PROPERTIES OF METALLIZED
SILICA GELS AND THEIR CATALYTIC ACTIVITY
IN THE SIMPLE OXIDATION REACTIONS



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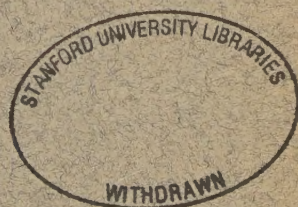
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THE ADSORPTION OF GASES BY METALLIZED SILICA GELS¹

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The problem of specific adsorption has attracted considerable attention in recent years. The work of Langmuir and Harkins has focused attention upon molecular orientation at surfaces while the work of Taylor and his colleagues at Princeton has been correlating adsorption and catalytic activity. Considerable work has been published on specific adsorption as well as the large amount of work which has appeared on non-specific adsorptions such as adsorptions by charcoals and silica gel. The following investigation was begun with the view of studying specific adsorption by metals using silica gel as the support material and later using the information in catalytic studies.

In the case of the metallized silica gels the adsorption of gases would in general be that of silica gel itself plus any specific adsorption which might be due to the metals which has been deposited as films on the surfaces of the gel itself. This would be true provided the deposition of metal did not appreciably cut down the effective surface for adsorption on the one hand. On the other hand it is barely possible that the deposition of metals might actually increase the total surface available for adsorption. Certain experiments reported in this paper give evidence that the extension of surface plays no important role. The results indicate that specific adsorptions may be superimposed upon non specific adsorptions.

Experimental

The metallized gels used in this investigation were prepared according to the method of Latshaw and Reyerson². After reduction by adsorbed hydrogen the metallized gels were dried at 110° in an atmosphere of hydrogen. In the case of the copper-treated gel it was found necessary to complete the reduction in hydrogen at higher temperatures since the first reduction seldom reduced the cupric ion below the cuprous condition. Adsorptions were measured for silica gel and silica gel metallized with silver, copper, platinum and palladium respectively. Adsorption isotherms were obtained for oxygen, carbon monoxide, carbon dioxide, methane and ethylene upon silverized gel at various temperatures. In the cases of platinized, palladized and copperized gels, the adsorption of hydrogen and sulphur dioxide was also measured. The adsorption measurements were carried out in an apparatus as shown in Fig. 1. Briefly the apparatus consisted of an adsorption bulb, A, connected by glass tubing to a mercury manometer, B, and a water-jacketed gas-measuring burette, C. This system was connected to the evacuating system by glass tubing with a stop cock at E. The gas burette was 50 cc. capacity and it was

¹ The work described in this paper formed part of a thesis submitted to the Graduated Faculty of the University of Minnesota by L. E. Swearingen in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June 1926.

² J. Am. Chem. Soc., **47**, 610 (1925).

graduated to tenths of cubic centimeters. Mercury was used as the confining liquid in this burette. A vacuum was produced in the system by a Stimpson double suction mercury vapor pump, supported by a Cenco Hy Vac pump. A McLeod gauge for measuring pressure was sealed directly into the glass mercury pump.

The gases used in the adsorption measurements were obtained and purified in the following manner. The nitrogen used in the early part of the work was prepared by heating a solution of equal parts of sodium nitrite, ammonium sulphate and sodium dichromate. The gas was passed over heated copper turnings to remove any oxygen and then collected and stored over water. Before use the gas was dried by passing it through concentrated sulphuric acid and then through a tube containing phosphorus pentoxide. Later in the work a tank of nitrogen was obtained that analyzed 99.7% nitrogen. This gas was first passed through alkaline pyrogallol and then dried as above before use.

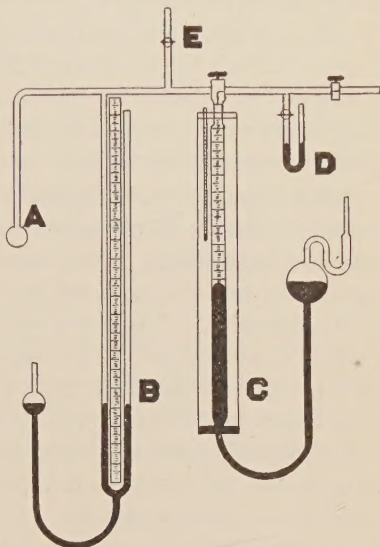


FIG. 1

Carbon monoxide was prepared, as needed, by the interaction of sulphuric and formic acids. The sulphuric acid was heated, in a suitable container, on a steam bath and the formic acid was admitted by means of a separatory funnel. The gas was bubbled through a solution of potassium hydroxide and then through concentrated sulphuric acid. It was finally dried over phosphorus pentoxide before use.

The carbon dioxide was obtained from a tank of commercial gas. It was adsorbed more than 99% by a solution of potassium hydroxide. The gas was dried over sulphuric acid and then passed through a tube containing granules of anhydrous calcium chloride.

The oxygen used was taken from a tank of compressed oxygen. It was adsorbed more than 99% by an alkaline solution of pyrogallol. It was dried by bubbling twice through concentrated sulphuric acid.

The hydrogen was obtained from a tank of electrolytic hydrogen. The gas was passed through a solution of alkaline pyrogallol and then through a tube containing some platinized silica gel. This tube of gel was heated to 120° to 130°. It had been previously found that the platinized gel would cause small percentages of oxygen to combine completely with hydrogen at these temperatures. The hydrogen was finally dried over phosphorus pentoxide.

The methane used was obtained from the Carbide and Carbon Chemical Corporation and was taken as needed from a tank of the compressed gas. The gas was washed with water, passed through a solution of alkaline pyrogallol,

and then dried by bubbling twice through concentrated sulphuric acid. The ethylene was used from a tank of compressed gas which had been prepared commercially for anaesthesia. Analysis showed it to be 97% pure. It was for our purposes washed successively with water, sulphuric acid, and a solution of potassium hydroxide. It was finally dried over sulphuric acid.

The helium which was used to determine the volume of the bulb was obtained through the courtesy of the Bureau of Mines. The sample as obtained contained about 94% of helium. The principal impurity was nitrogen. The impurities were adsorbed by passing the gas through a tube of cocoanut charcoal immersed in liquid air.

The adsorption measurements were made in essentially the following manner. A sample of the gel was first weighed into the adsorption bulb, A, and the bulb sealed to the apparatus. Before making adsorption measurements the entire apparatus was washed with the gas whose adsorption was to be measured. An exception to this procedure was made in the case of carbon monoxide and the platinized gel. The preliminary washing was omitted in this case because the work of Taylor and Burns¹ had shown that the adsorption of carbon monoxide by platinum had been reduced by about 63% following an initial treatment with carbon monoxide. The bulb containing the gel sample was then immersed in an oil bath which was heated to 200°, and the evacuating pumps started. In order to obtain consistent results it was necessary to adopt a uniform procedure. The bulb was heated at 200° for a period of three hours and the vacuum pumps were operated continuously during the entire period. During the process of evacuation the gas burette would be filled with the gas which was to be adsorbed. After remaining in the burette for about two hours, the gas volume, the temperature of the water jacket and the barometric pressure were recorded. By means of the leveling tube, D, a fine adjustment to atmospheric pressure could be obtained in determining the volume of the gas in the burette.

Upon completion of the evacuation process, stop-cock, E, was turned so that the connection to the pumps was broken. The oil bath was removed and the bulb brought to the temperature at which the adsorption was to be measured. Adsorptions were measured at the following temperatures: 0°, 64.5°, 100°, 138° and 218°. At 0° finely cracked ice mixed with water was used in a Dewar flask. Boiling methyl alcohol was used for the temperature of 64.5°, boiling water at 100°, boiling xylene at 138°, and boiling naphthalene at 218°. In each case these liquids were contained in large flasks equipped with reflux condensers and in no case was the adsorption bulb permitted to come in contact with the boiling liquid, but it was bathed in the vapors from the liquid. After the adsorption bulb and contents had reached temperature equilibrium, the manometer was read and gas admitted from the gas burette through the stop-cock at the top of the burette. The gas was added in small quantities, the successive additions being made only after the manometer indicated that equilibrium had been reached. Three successive readings at

¹ J. Am. Chem. Soc., **43**, 1273 (1921).

fifteen minute intervals, which showed no change, were taken as indicating the establishment of equilibrium. The total volume of gas added, the temperature and pressure at which the added volume was measured, together with the manometer reading, were all recorded. The extent of adsorption at different pressures could readily be obtained from this data together with a knowledge of the free space in the bulb. Gas volumes were always corrected to standard conditions.

During the early part of the work, nitrogen was used to determine the free space in the bulb. The capacity of each bulb and gel sample was determined prior to the adsorption study and the adsorption of gas was taken as the difference between this volume at the several pressures and the volume of gas admitted at the given pressure, all volumes being changed to standard conditions. Later a comparison was made between the volume of a bulb as determined by nitrogen and the volume as determined by helium. In these cases silica gel was used in the bulb and two separate measurements were carried out. In one case helium was used to fill the bulb and then removed and nitrogen admitted. In the other case the gases were used in the reverse order. No difference in total volumes could be observed with the reversal of the order of admission. The comparative data for a set of measurements are given in Table I.

TABLE I

Comparative Data on the Adsorption of Helium and Nitrogen by Silica gel at 0°

Pressure in millimeters of Mercury	Volume (standard conditions) of gas admitted	Pressure in millimeters of Mercury	Volume (standard conditions) of gas admitted
Helium		Nitrogen	
40.0	1.55 cc	45.0	1.70 cc
92.0	4.00 cc	142.0	5.60 cc
160.5	6.05 cc	238.0	9.15 cc
330.0	13.00 cc	348.0	13.70 cc
540.0	20.40 cc	528.5	21.05 cc
732.8	28.10 cc	745.7	28.90 cc

If the volumes of gas are plotted against pressure it will be found that the adsorptive capacity of the gel for nitrogen and helium is essentially the same for all pressures at 0°. The maximum divergence occurs at a pressure of one atmosphere (extrapolated) and here the difference is less than 0.70 c.c. As a result of this work corrections were made to bring the value of free space to that determined by helium. The adsorption measurements in this investigation were carried out in duplicate.

Results

Table II gives a typical set of adsorption measurements and is experiment 45 in the series.

Figs. 2 and 3 show the adsorption isotherms obtained by plotting amounts adsorbed as ordinates against the pressures as abscissas. From such curves

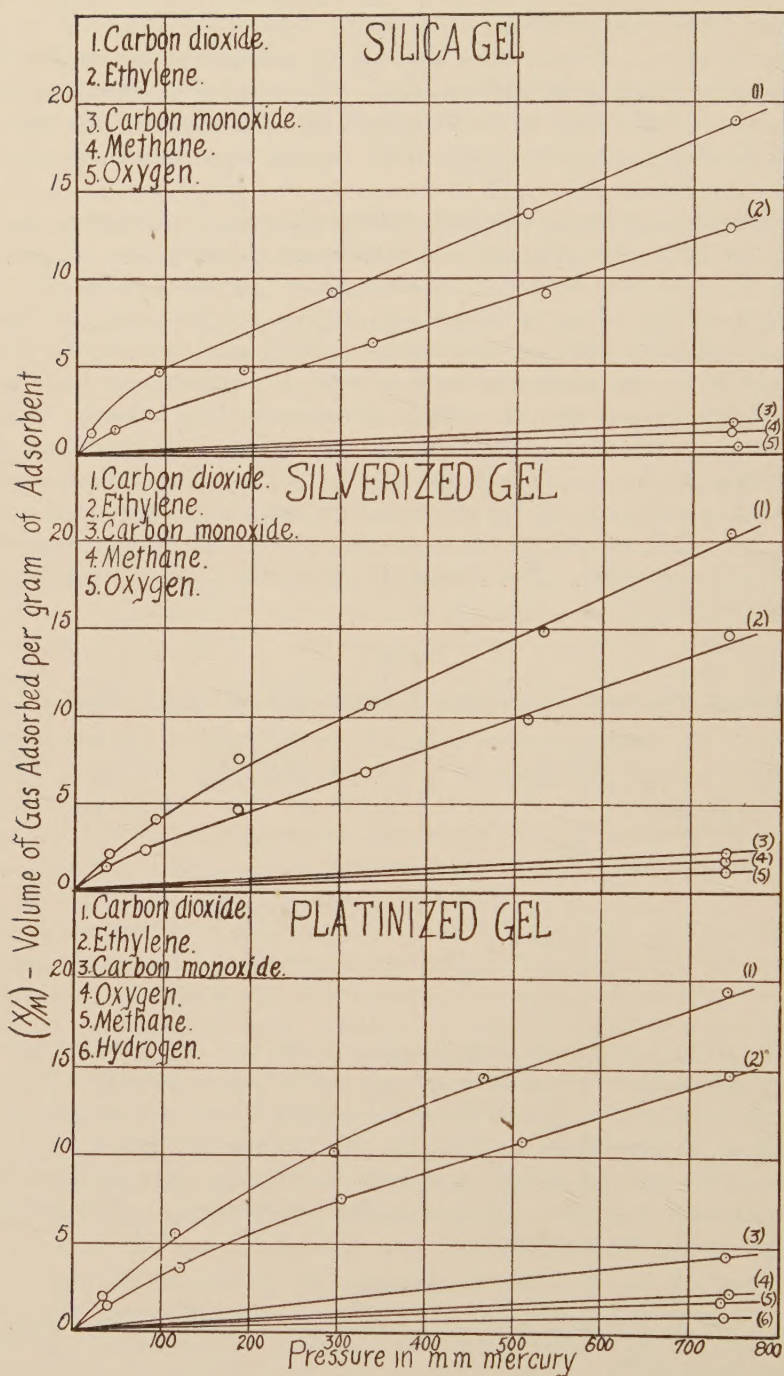


FIG. 2
Adsorption Isotherms at 0°

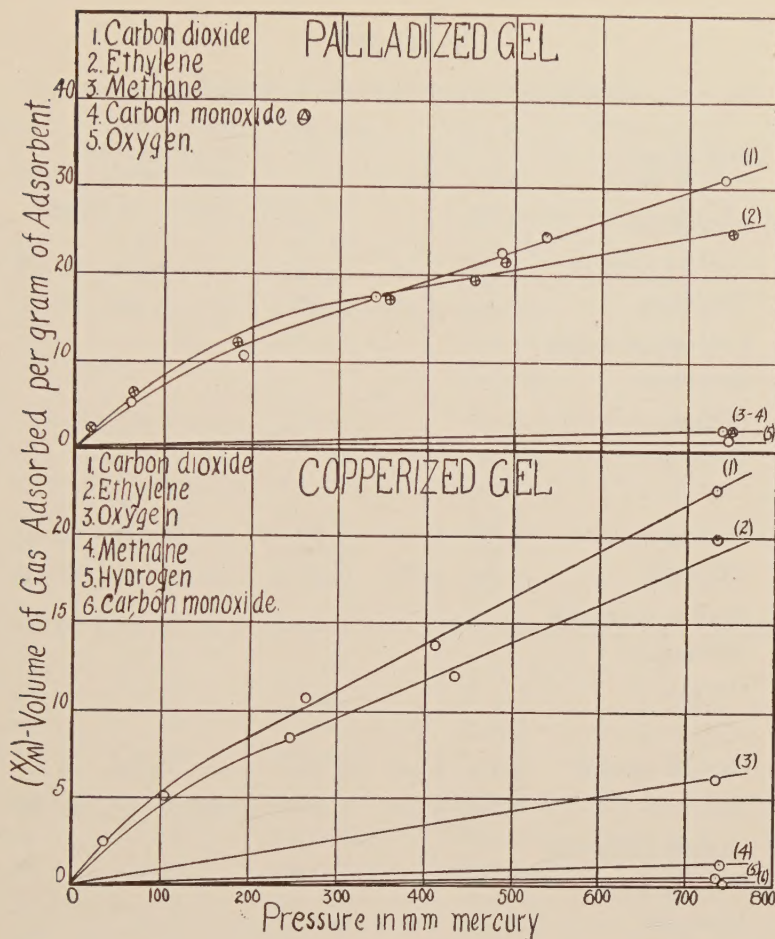


FIG. 3
Adsorption Isotherms at 0°

as these the data presented in Table III were obtained. These data give the equilibrium values at 0°. In addition to measurements at 0°, adsorptions of carbon dioxide, ethylene and sulphur dioxide were made at temperatures ranging from 0° up to 218° as indicated previously. Table IV gives the adsorption equilibrium values at actual atmospheric pressures at the time of measurement.

TABLE II
Adsorption of Ethylene by Palladized Gel at 0°

Pressure in mm. Mercury	Volume of gas admitted (cc. at standard conditions)	Free space from the helium value	X/M
20.20	3.80	.85	2.95
95.20	10.70	4.02	6.68
225.20	22.40	9.50	12.90
455.00	38.58	19.15	19.43
749.50	56.68	31.60	25.08

TABLE III

Cubic centimeters of gas adsorbed at the indicated pressures at 0°

Equilibrium Pressure in m.m. of Hg.		100	200	300	400	500	600	700
Adsorbent	Adsorbate							
	Carbon dioxide	4.98	7.15	9.25	11.45	13.65	15.70	17.80
	Ethylene	2.51	4.20	5.80	7.45	9.00	10.60	12.25
Silica	Carbon monoxide							1.80
Gel	Methane							1.35
	Oxygen							0.50
	Hydrogen							0.25
	Carbon dioxide	4.25	7.30	9.80	12.20	14.55	16.80	19.20
	Ethylene	2.80	4.60	6.40	8.20	10.00	11.70	13.50
Silverized	Carbon monoxide							2.30
Gel	Methane							1.80
	Oxygen							1.20
	Carbon dioxide	4.65	8.00	10.75	13.00	14.80	16.60	18.45
	Ethylene	2.60	5.50	7.40	9.20	10.65	12.40	13.95
Platinized	Carbon monoxide							4.35
Gel	Oxygen							2.40
	Methane							1.85
	Hydrogen							1.00
	Carbon dioxide	7.20	12.30	15.90	19.30	23.00	26.20	29.60
	Ethylene	8.40	14.00	17.00	18.80	20.70	22.70	24.40
Palladized	Methane							2.10
Gel	Carbon monoxide							2.10
	Oxygen							1.00
	Carbon dioxide	5.30	8.50	11.20	13.90	16.50	19.20	21.85
	Ethylene	4.50	7.45	9.60	11.85	14.00	16.15	18.40
Copperized	Oxygen							6.00
Gel	Methane							1.40
	Hydrogen							0.60
	Carbon monoxide							0.25

TABLE IV
Effect of Temperature on Adsorptions

Pressure in m.m. Mercury	X/M c.c. adsorbed per gram of adsorbent	Temperature	Pressure in m.m. Mercury	X/M c.c. adsorbed per gram of adsorbent	Temperature
Ethylene on Silica Gel			Ethylene on Silverized Gel		
746.50	13.62	0.00°	742.00	14.74	0.00°
746.50	5.32	64.50	742.70	6.69	64.50
746.50	3.77	100.00	742.70	4.56	100.00
746.50	0.00	218.00	742.70	2.86	138.00
			742.80	0.00	218.00
Carbon Dioxide on Silica Gel			Carbon Dioxide on Silverized Gel		
747.50	19.03	0.00°	744.80	20.46	0.00°
747.50	5.66	64.50	744.00	7.46	64.50
748.50	2.56	100.00	744.00	4.32	100.00
748.00	1.78	138.00	744.00	2.86	118.00
748.00	0.00	218.00	743.90	0.00	238.00
Carbon Dioxide on Platinized Gel			Carbon Dioxide on Copperized Gel		
735.00	18.80	0.00°	7.3300	22.75	0.00°
735.00	4.38	64.50	7.3300	6.95	64.50
736.00	.50	100.00	7.3350	3.02	100.00
736.50	0.00	138.00	7.3340	.52	138.00
Ethylene on Platinized Gel			Sulphur Dioxide on Palladized Gel		
739.50	14.38	0.00°	749.00	136.38	0.00°
739.00	5.73	64.50	749.00	34.73	64.50
739.50	2.63	100.00	749.20	20.80	100.00
739.50	.93	138.00	739.20	10.00	138.00
			749.40	2.64	218.00
Sulphur Dioxide on Platinized Gel			Ethylene on Copperized Gel		
739.71	100.86	0.00°	735.50	20.30	0.00°
739.40	30.80	64.50	735.00	4.65	64.50
740.00	12.01	100.00	736.00	.67	100.00
740.00	7.31	138.00			
740.00	1.30	218.00	Sulphur Dioxide on Copperized Gel		
			750.00	143.21	0.00°
			750.00	41.65	64.50
			749.00	21.20	100.00
			749.00	11.70	137.00
			749.00	6.20	218.00

In addition to the forgoing measurements it was thought desirable to study the effect of increasing the metal content on the adsorptive capacity of gels. Accordingly, adsorptions of carbon dioxide, carbon monoxide and ethylene were obtained upon platinized gels Nos. 1, 2, 3, and 4. Platinized

gel 1 contained the platinum from a single reduction, platinum gel 2 contained the platinum from two complete successive reductions by adsorbed hydrogen, No. 3 was subjected to three reductions and No. 4 contained the platinum from four reductions. These measurements were made at 0°. Table V gives the adsorption values for the four platinized gels.

TABLE V
ADSORPTION MEASUREMENTS ON PLATINIZED GEL 1

Pressure in m.m. Mercury	Vol. of gas admitted (c.c. N.T.P.)	Free space from the Helium value	X/M
Ethylene			
34.00	2.70	1.31	1.39
94.00	7.20	3.63	3.57
214.00	15.20	8.25	6.95
372.00	24.80	14.35	10.45
553.00	35.68	20.60	15.08
735.70	46.17	28.40	17.77
Carbon Dioxide			
41.50	4.00	1.60	2.40
105.50	9.60	4.07	5.53
197.50	16.50	7.63	8.87
351.45	26.50	13.55	12.95
604.50	42.75	23.35	19.40
Carbon Monoxide			
59.90	3.10	2.30	.80
161.50	7.50	6.24	1.26
340.50	14.75	13.15	1.60
509.50	22.00	19.70	2.30
743.00	31.90	28.70	3.20

ADSORPTION MEASUREMENTS ON PLATINIZED GEL 2

Ethylene			
32.50	2.80	1.25	1.55
82.50	6.70	3.16	3.54
206.50	14.35	7.90	6.45
394.50	25.65	15.15	10.50
752.00	44.62	28.90	15.72
Carbon Dioxide			
37.00	2.95	1.43	1.52
111.00	7.45	4.28	3.17
194.00	13.95	7.50	6.45
374.00	25.75	14.50	11.25
684.00	44.71	26.40	18.31
Carbon Monoxide			
45.00	2.55	1.71	.84
166.00	7.65	6.41	1.24
350.00	15.55	13.50	2.05
748.00	32.25	28.90	3.35

TABLE V Continued

Pressure in m.m. Mercury	Vol. of gas admitted (c.c. N.T.P.)	Free space from the Helium value	¹⁸ X/M
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ADSORPTION MEASUREMENTS ON PLATINIZED GEL 3

Ethylene

33.50	3.60	1.29	2.31
105.00	8.65	4.06	4.59
254.00	17.80	9.80	8.00
428.00	29.35	16.50	12.85
746.40	46.55	28.80	17.75

Carbon Dioxide

33.50	3.62	1.30	2.32
108.00	8.60	4.00	4.60
163.50	12.75	6.30	6.45
316.40	22.30	12.20	10.10
668.00	43.58	25.80	17.78

Carbon Monoxide

50.50	2.95	1.95	1.00
159.50	7.76	6.16	1.60
301.50	13.65	11.64	2.01
489.50	22.08	18.88	3.20
733.00	32.02	28.40	3.62

ADSORPTION MEASUREMENTS ON PLATINIZED GEL 4

Ethylene

33.00	2.80	1.27	1.53
99.00	7.40	3.83	3.57
200.00	14.20	7.72	6.48
323.10	21.50	12.50	9.00
412.00	27.85	15.90	11.95
754.40	46.78	29.10	17.68

Carbon Dioxide

38.00	3.90	1.45	1.45
98.00	8.20	3.76	4.44
240.50	17.60	9.24	8.36
378.00	26.08	14.50	11.58
681.00	43.48	26.15	17.33

Carbon Monoxide

100.50	4.76	3.86	.90
240.40	11.17	9.22	1.95
428.80	18.30	16.40	2.90
745.00	32.60	28.60	4.00

Discussion of Results

To facilitate the comparison of results for the adsorption of the various gases upon the metallized gels, the adsorptions of the gases by the gels at 0° and 760 m.m. pressure has been tabulated in Table VI. The values at 760 m.m. pressure were obtained by extrapolation of the adsorption isotherms from the final equilibrium pressure which was the actual atmospheric pressure observed at the time of measurement.

TABLE VI
Comparative Data on Adsorptions by Different Gels

Gas Adsorbed	Boiling Point (Absolute temperature)	X/M for Silica Gel	X/M for Silverized Gel	X/M for Palladized Gel	X/M for Platinized Gel	X/M for Copperized Gel
H ₂	20.4	0.25	—	0.00	1.10	0.55
CO	81.1	1.60	2.75	2.60	4.60	0.40
O ₂	90.10	0.45	1.35	2.00	2.60	6.40
CH ₄	111.4	1.75	2.20	2.40	2.05	1.40
C ₂ H ₄	169.3	12.70	14.50	26.00	15.10	20.40
CO ₂	194.6	19.40	20.70	32.00	19.60	23.00
SO ₂	263.1	—	—	132.35	102.00	160.00

In the case of silica gel itself the increasing order of adsorption, with the exception of carbon monoxide, follows the increase in the boiling point. In the case of ethylene and carbon dioxide excellent adsorption isotherms were obtained. Little tendency to reach a maximum adsorption was observed in the case of these gases for the range of pressure studied. This is characteristic of nonspecific adsorptions. The adsorption of carbon dioxide is considerably higher than the values obtained by Patrick, Owens and Preston.¹ Above 200 m.m. pressure however, the two isotherms have the same ratio to each other. The difference between these values and those of Patrick, Owen and Preston can be attributed to differences in the water content of the gel and possibly the difference in granule size.

The Freundlich equation for adsorption was found to fit the data whenever there was considerable adsorption. This was also true for the adsorptions on the metallized gels. If the logarithms of the pressures are plotted as abscissas and logarithms of x/m plotted as ordinates, a straight line will result if the values fit the Freundlich equation. This is true for the data here presented.

The adsorption of the gases by the silverized gel show an increase in all cases. The order of adsorption as compared to the boiling points has not changed when compared to silica gel. Per gram of adsorbent ethylene shows the largest increase, 1.80 c.c. more of ethylene being adsorbed by the silverized gel than by the silica gel alone. On the basis of ratio increase however, oxygen and carbon monoxide are more strongly adsorbed by silverized gel than are the other gases. If we assume that the increase for carbon dioxide

¹ J. Am. Chem. Soc., **43**, 1273 (1921).

is due to change in gel structure alone, then on the basis of this ratio increase, the presence of silver in the gel has resulted in the specific adsorption of oxygen, carbon monoxide and possibly ethylene and methane.

The adsorption values for the palladized gel are not strictly comparable to the other adsorptions because the silica gel which was used was from a second preparation of the gel. It shows distinctly greater adsorptive capacity for carbon dioxide. This may be attributed largely to gel structure since Taylor and Burns¹ have shown that palladium adsorbs carbon dioxide but slightly. If we make this assumption then by comparison with the data on the first silica gel the gel containing the palladium should adsorb 2.63 c.c. of carbon monoxide, 0.74 c.c. of oxygen, 2.88 c.c. of methane and 20.90 c.c. of ethylene. We find good agreement between these calculated values and the observed results in the case of carbon monoxide and methane. Oxygen seems to be specifically adsorbed by the palladium and there is not much doubt that ethylene is very strongly adsorbed, since there is an adsorption of more than 5 c.c. above the calculated value. Specific adsorption of ethylene by the palladized gel is further indicated by the shape of the adsorption curve. More ethylene is adsorbed at low pressures than carbon dioxide while the carbon dioxide is more strongly adsorbed near atmospheric pressures. This type of curve is a characteristic of specific adsorptions.

In the case of hydrogen the first experimental work indicated zero adsorption. This might be due to two separate factors. Either the drying in an atmosphere of hydrogen filled the palladized gel with hydrogen and this was not subsequently removed by the heating and evacuation, or the palladium surface had become poisoned as regards hydrogen adsorption. Taylor and Burns² have shown that palladium exhibits considerable reluctance in giving up hydrogen so that the first explanation is plausible. Additional work seems to eliminate this possibility in these experiments. Pollard³ has shown that traces of grease poison platinum as far as adsorption of hydrogen is concerned. Accordingly, additional experiments were carried out using the utmost precaution to keep grease away from the palladized gel. The palladized gel then showed an adsorptive capacity of 0.76 c.c. of hydrogen per gram of metallized gel at 0° and 760 m.m. pressure. A repetition of the adsorption measurements decreased the adsorption to 0.55 c.c. per gram of gel. A second set of experiments was then carried out. The palladized gel was first heated in an atmosphere of nitrogen at 120°-140° for a period of four hours. It was felt that this might partially remove any adsorbed hydrogen. The regular procedure for adsorption study was then carried out. The adsorption determined in this experiment gave a value of 0.87 c.c. per gram of the metallized gel. This is so close to the value previously obtained that no further work was done on this phase of the problem. It would appear from these results that palladium is also very easily poisoned as far as hydrogen adsorption is concerned. An

¹ J. Am. Chem. Soc., **29**, 421 (1925).

² J. Am. Chem. Soc., **43**, 1273 (1921).

³ J. Phys. Chem., **27**, 356 (1923).

adsorption of 0.87 c.c. of hydrogen per gram of palladized gel does not indicate a marked specific adsorption of hydrogen by the palladium present in the gel.

The platinized gel was prepared upon the same silica gel as was used in all of the work except the palladized gels. It is evident from the adsorption values that there is no longer much relation between amounts adsorbed and boiling points of the substances adsorbed. The amount of carbon dioxide adsorbed is the same as for silica gel itself. The presence of platinum in the gel has considerably increased the capacity of the gel to take up ethylene. The adsorption of methane has not greatly increased. However, in the cases of hydrogen, oxygen, and carbon monoxide the platinized gel is able to adsorb from three to five times as much gas as the silica gel. The marked adsorption of carbon monoxide fits well with the experiments of Pollard and the adsorption of hydrogen, oxygen, and carbon monoxide agrees well with the work of Taylor and Burns on platinum black.

The copperized gel shows very different adsorptive capacity when compared to the other adsorbents. There is less carbon monoxide and methane adsorbed than for the unmetallized gel. Hydrogen is about twice as strongly adsorbed while large increases are noted for the other gases. About thirteen times as much oxygen is adsorbed as for the gel itself and this may even mean reaction of the copper film with oxygen. It is evident that the copper in the gel specifically adsorbs oxygen and ethylene and perhaps hydrogen, carbon dioxide and sulphur dioxide.

The effect of temperature upon the adsorption of the gases is the same as expected. Increased temperature rapidly cuts down the adsorption. It should be noted however that the gases which are specifically adsorbed are still slightly adsorbed at a higher temperature than those not specifically adsorbed.

The effect of successive metallizations by platinum does not show any great change except in the case of carbon monoxide where a steady increase in amount adsorbed is noted in going from the singly metallized gel to that metallized four times. This tends to confirm the point of view that carbon monoxide is adsorbed specifically by platinum. In the case of ethylene a lowering of the adsorptive capacity is noted for the case of the gel twice metallized and then there is a slight increase over this value for the gels metallized three and four times. Specific adsorption by the platinum may be overcoming the filling of the capillaries in the gel by the metal.

Summary

1—The adsorption of gases upon silica gels metallized with silver, copper, platinum and palladium has been measured.

2—Hydrogen is adsorbed appreciably more upon the copper, platinum and palladium treated gels.

3—Carbon monoxide is specifically adsorbed by all the metallized gels except copper.

4—Oxygen is very specifically adsorbed by the copperized gel. The other metallized gels also exhibit specific adsorption for oxygen.

5—There appears to be no marked specific adsorption of the gels for methane.

6—The metallized silica gels all adsorb ethylene more strongly than does silica gel.

7—The adsorption of carbon dioxide gives little evidence of a specific effect except perhaps in the case of copper.

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THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS

III. The Synthesis of Water

BY L. E. SWEARINGEN AND L. H. REYERSON

Ever since Sir Humphry Davy in 1817 observed that a platinum wire heated below redness, promoted the combination of hydrogen and oxygen, the catalytic synthesis of water has been the subject of much investigation. Because of the relatively simple mechanism of water synthesis it was felt that a study of this reaction would give some idea concerning the catalytic activity of metallized silica gels in oxidation reactions. Morris and Reyerson¹ have shown that metallized silica gels exhibit marked catalytic activity in hydrogenation reactions. Furthermore x-ray studies² have shown that when the metal is deposited upon the surface of the silica gel by the method described, it exists in a very fine state of division. A very large number of active catalytic centers undoubtedly exist under these conditions and the catalysts should exhibit marked activity in oxidation reactions.

Experimental

The metallized silica gels used in this research were the same as those used in the adsorption studies previously reported.³ The gases were streamed at rates varying from 15 to 300 cc. per minute through an apparent volume of 5 cc. of catalyst. The tube carrying the catalyst was maintained in a constant temperature bath and the temperature of the bath was varied from -17° in the case of the platinized and palladized gels to 290° for the copper and silver catalysts. The gas mixtures contained from about six to nine per cent of oxygen, fifty percent hydrogen and the remainder nitrogen.

A gas mixture of approximately the desired composition was first collected in a 20 liter glass bottle. Water was used as the confining liquid. After shaking and allowing to stand for several hours, a sample of the gas mixture was analysed. The gas mixture was then ready for use. An inverted glass bottle full of water supplied the pressure necessary to force the gas mixture through the catalyst train. By regulating the flow of water from the upper to the lower bottle, the velocity of the gas through the catalyst could be varied over a wide range. On leaving the container the gas mixture passed a pressure regulator which was adjusted to just allow gas to escape through it. The gas was then metered by a flow-meter which had been previously calibrated. The gas was dried before entering the catalyst tube by passing through a calcium chloride tube. Metallized gel granules having an apparent volume of 5 cc. were placed on a deep U tube which was similar to the tube described by Morris and Reyerson. A thermometer was kept imbedded in

¹ Morris and Reyerson: *J. Phys. Chem.*, **31**, 1220 (1927).

² Reyerson, Harder and Swearingen: *J. Phys. Chem.*, **30**, 1623 (1926).

³ Reyerson and Swearingen: *J. Phys. Chem.*, **31**, 88 (1927).

the catalyst in order to note any rise in the temperature of the catalyst above that of the bath in which the catalyst tube was immersed. On leaving the catalyst tube the gas was first bubbled through a wash-bottle containing water in order to cool the gases and then led into the gas analysis apparatus. This was a modified Orsat apparatus. It contained absorption pipettes filled with small glass tubes and a water-jacketed gas-measuring burette of 100 cc. capacity. The manifold of the Orsat apparatus was closed with two-way stop cocks in such a manner that the gases flowing from the catalyst could be passed through the manifold by-passed around it. Except during analysis the gas flowed continuously through the manifold. The burette and pipettes were separated from the manifold by glass stop cocks. In this investigation the oxygen content of the gas mixture was the only thing determined. The oxygen was absorbed in an alkaline solution (1500 gm. of KOH per liter of water) of pyrogallol containing 10 gm of pyrogallol acid per 100 gm. of solution.

The catalyst tube was kept immersed in a bath for temperature control. Above 150° solder metal was used, between 100° and 150° Wood's metal was used and below 100° water or ice and ice salt mixtures were used. The bath was well insulated and constant temperatures could be maintained to within a degree or two at the higher temperatures. The temperature was always taken at the time of sampling for analysis.

Experiments were carried out showing the effect of temperature on the combination of hydrogen and oxygen in the presence of the copper and silver gel catalysts. Since the reaction was practically complete at all temperatures in the case of the platinized and palladized gels when the rate of flow was low, a study was made of the efficiency of the catalysts at various rates of flow for several temperatures.

Results

The results of the experimental work are presented in Tables I to IV. When two columns are given under the heading temperature, the column to the left gives the temperature of the bath in which the catalyst tube is immersed while the column to the right gives the temperature as recorded by the thermometer imbedded in the catalyst. In the cases where only one column is given, the temperature recorded was that of the bath. This also indicated that the thermometer in the catalyst recorded the same temperature as that in the bath. Fig. 1 shows graphically the effect of temperature upon the efficiency of copper and silver catalysts in promoting the water synthesis. The rates of flow were low. Fig. 2 illustrates the effect of changing the rate of flow on the efficiency of the more active platinum and palladium catalysts. Three temperatures are given for each catalyst, and the temperatures are those of the bath surrounding the catalyst tube.

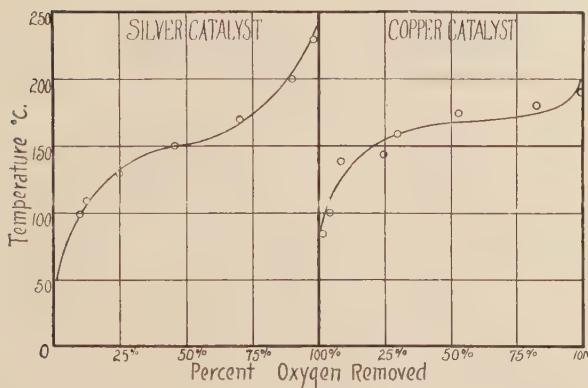


FIG. 1
Effect of Temperature on Combination of H_2 and O_2

TABLE I
Silver Catalyst

Gas Mixture: 6.50% Oxygen, 50.00% Hydrogen, 43.50% Nitrogen.

Temperature	Rate of Flow, cc. per Minute	Percent Oxygen in Residual Gas	Percent Oxygen removed
300	24	0.00	100.00
260	24	0.00	100.00
230	24	0.00	100.00
230	24	0.20	97.00
225	24	0.20	97.00
224	24	0.00	100.00
218	24	0.20	97.00
202	24	0.41	94.20
200	24	0.60	90.80
187	24	0.80	87.70
182	24	1.00	84.60
170	24	1.95	70.00
150	24	3.00	46.20
133	24	4.80	26.20
122	24	4.87	25.10
110	24	5.60	13.85
100	24	5.80	10.75

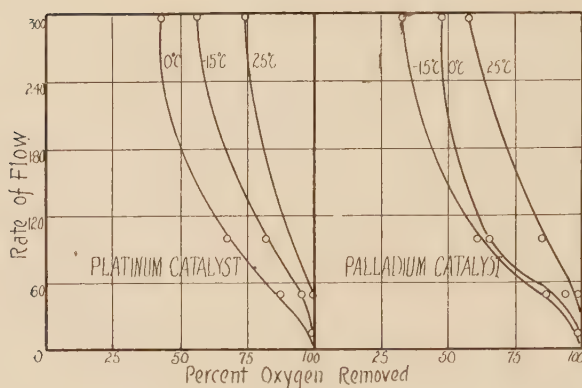


FIG. 2
Effect of Rate of Flow on the Combination of H_2 and O_2

TABLE II

Copper Catalyst

Gas Mixture: 7.00% Oxygen, 50.00% Hydrogen, 43.00 Nitrogen.

Temperature	Rate of Flow, cc. per Minute	Percent Oxygen in Residual Gas	Percent Oxygen removed
195	38	0.00	100.00
175	38	2.93	58.20
174	38	3.57	49.00
151	38	5.42	22.60
143	38	5.13	26.75
141	38	5.44	22.30
124	38	6.35	9.30
100	38	6.44	8.00
220	38	0.00	100.00
200	38	0.00	100.00
197	28	0.00	100.00
192	38	0.00	100.00
185	38	1.34	83.40
174	38	1.49	81.25
166	38	5.54	30.80
155	38	5.70	28.80
140	38	6.73	15.90
110	38	7.34	7.50
90	38	7.70	3.75
80	38	7.67	4.15

TABLE III
Platinum Catalyst

Gas Mixture: 9.20% Oxygen, 50.00% Hydrogen, 40.80% Nitrogen.

Temperature		Rate of Flow	Percent Oxygen	Percent Oxygen
		cc. per Minute	in Residual Gas	removed
Bath	Catalyst			
24	25	15	0.00	100.00
24	25	15	0.00	100.00
24	25	15	0.00	100.00
24	26	50	2.21	76.00
24	27	50	1.61	82.50
24	26	50	0.00	100.00
24	26	50	0.00	100.00
24	26	50	0.00	100.00
25	38	300	2.13	77.00
25	38	300	2.50	73.00
25	36	300	2.59	71.80
0	6	15	2.51	71.30
0	7	15	0.16	99.00
0	4	15	0.00	100.00
0	7	15	0.00	100.00
0	8	50	0.83	90.00
0	9	50	1.21	86.00
0	9	50	1.00	88.00
0	12	100	3.10	64.50
0	10	100	2.57	70.50
0	10	100	2.65	69.50
0	14	300	4.78	45.00
0	15	300	4.93	43.40
0	15	300	4.80	44.80
-16	-10	15	4.55	48.50
-16	-10	15	0.00	100.00
-16	-10	15	0.00	100.00
-16	-10	15	0.00	100.00
-15	0	50	0.28	96.80
-15	-5	50	0.27	96.90
-15	0	50	0.30	96.60
-15	5	100	1.67	81.00
-15	5	100	1.56	82.00
-15	4	100	1.50	82.70
-15	15	300	3.78	56.60
-15	15	300	3.83	56.10
-15	16	300	3.90	55.20

TABLE IV

Palladium Catalyst

Gas Mixture: 9.20% Oxygen, 50.00% Hydrogen, 40.80% Nitrogen.

Temperature		Rate of Flow, cc. per Minute	Percent Oxygen in Residual Gas	Percent Oxygen removed
Bath	Catalyst			
25	26	15	0.00	100.00
25	26	15	0.00	100.00
25	26	15	0.00	100.00
25	26	50	0.00	100.00
25	26	50	0.00	100.00
25	28	50	0.00	100.00
25	28	50	0.00	100.00
25	33	100	1.75	81.00
25	36	100	.87	90.50
25	35	100	1.20	87.00
25	40	300	3.93	57.30
25	41	300	3.88	57.80
25	41	300	3.80	58.80
0	2	15	0.00	100.00
0	2	15	0.00	100.00
0	3	15	0.00	100.00
0	10	50	0.71	92.40
0	8	50	0.42	95.50
0	9	50	0.56	94.00
0	16	100	3.19	65.40
0	17	100	3.06	66.80
0	16	100	3.00	67.49
0	21	300	4.56	50.40
0	20	300	4.92	46.60
0	21	300	4.78	48.10

Gas Mixture: 8.70% Oxygen, 50.00% Hydrogen, 42.30% Nitrogen.

-17	-4	15	0.00	100.00
-17	-5	15	0.00	100.00
-16	-5	15	0.00	100.00
-17	0	50	1.08	87.80
-16	0	50	0.85	90.50
-16	0	50	0.82	90.60
-15	0	100	3.50	60.00
-16	0	100	3.30	62.00
-15	1	100	3.35	61.70
-15	5	300	5.67	34.90
-15	4	300	5.93	31.95
-15	6	300	5.80	33.35

Discussion of Results

In the case of the silverized gel, Table I and Fig. 1 show that the reaction became measurable at about 100° . The continuation of the curve indicates a reaction at still lower temperature but this was not realized in the experiments. The catalyst increases in efficiency as the temperature rises. The most rapid increase comes in the temperature interval between 140° and 180° . Above 200° practically all of the oxygen is removed at the rates of streaming studied.

The copper catalyst gives a measurable reaction at a lower temperature than the silver catalyst. The reaction is measurable at 80° . There is a rather steady increase in the amount of reaction until 165° is reached when there is a rapid rise in the efficiency of the catalyst. The catalyst becomes one hundred percent efficient below 200° for the rates of flow of the gas mixture studied. The curves for the silver and copper catalysts are much alike except that above 165° the efficiency of the copper catalyst increases more rapidly than does that of the silver catalyst. This copper catalyst compares favorably with the one prepared by Pease and Taylor.¹ In fact it probably initiates reaction at a slightly lower temperature.

The platinized and palladized gels on the other hand promote complete conversion of the oxygen and hydrogen at all of the temperatures studied provided the rate of gas flow was not too fast. Fig 2 shows the effect of increasing the rate at which the gas streamed through the catalyst upon the efficiency of the catalyst. The efficiency of the catalyst does not diminish as rapidly at the higher temperatures for given increases in gas flow as it does at lower temperatures. These catalysts heat up considerably as a result of the reaction and the temperature is undoubtedly much higher than that recorded by the thermometer immersed in the catalyst because the platinum catalyst was often observed to glow at local points. Tables III and IV show that increasing flow produces increasing differences between the temperature of the bath and that of the catalyst. The platinum catalyst shows a thirty degree rise in temperature at -15° for a streaming rate of 300 cc. per minute. This is the greatest difference observed in any of the experiments. The copper and silver catalysts show no differences in bath and catalyst temperature.

The most interesting result shown by these experiments is that the platinum catalyst is more efficient in promoting the synthesis of water at faster streaming rates than is the palladized gel. This is certainly true at 25° and at -15° . At 0° there is not much difference between the two catalysts. It would also appear that the platinized gel is more efficient at -15° than it is at 0° . This is probably due to the fact that at 0° the water formed by the reaction condenses in small droplets on the wall of the tube. These droplets tend to fall on the catalyst or run down the tube and onto the catalyst. Here the water is vaporized by the local heating of the catalyst granules and this steam tends to prevent the reacting gases from reaching the active surface.

¹ J. Am. Chem. Soc., **44**, 1637 (1922).

At -15° the water freezes on the walls of the tube and does not interfere with the reaction. This no doubt accounts for the almost equal efficiency of the catalysts at 0° while at the other temperatures the platinized gel is considerably more efficient. At slow rates of streaming both catalysts are sufficiently active to use up the oxygen.

The present study does not make it possible to postulate a mechanism of reaction on the catalyst surface because the composition of the gas mixture was not varied.

Summary

1. The silver catalyst initiates the reaction below 100° and is practically one hundred per cent efficient above 200° at the rate of streaming studied.
2. The copperized gel initiates the reaction below 80° and the reaction is complete below 200° .
3. The platinized and palladized gels show marked activity in promoting the synthesis of water at all temperatures studied. The platinized gel is more efficient than the palladium catalyst as the rate of streaming of the gases is increased.

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THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS

IV. The Oxidation of Methane

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A great many investigations have been carried out having as their basis the oxidation of methane. The researches of Bone and Wheeler and their co-workers are well known. In recent years Berl and Fischer¹ have studied the oxidation of methane at temperatures above 400°. They find small amounts of formaldehyde under certain conditions. Tropsch and Rollen² also studied this reaction passing the mixed gases through heated quartz tubes at rather rapid rates. The best results obtained by these investigators corresponded to a conversion of about six per cent of the total methane to formaldehyde. Because of the interest which attaches to the oxidation of methane it was thought that a study of the activity of metallized silica gels on this reaction might lead to interesting results in the field of partial oxidation of hydrocarbons.

Experimental

The same experimental procedure was used in this work and the same catalysts used as in the previous paper by the authors on the synthesis of water. A gas absorption pipette containing a solution of KOH was added to the gas analysis system to take care of the CO₂ formed by oxidation. The gases were streamed at rates varying from 15 cc. to 200 cc. per minute through an apparent volume of 5cc. of catalyst. The reaction was studied with the catalyst maintained at temperatures varying from 200° to 400°. The gases after reaction were analysed for carbon dioxide and oxygen. Preliminary experiments showed that the only oxidation product of methane present in analizable quantity was carbon dioxide.

Results

The results of the experiments are given in Tables I to IV and in Fig. 1. The symbols used have the following meaning:

- A—The percent of methane in the original mixture.
- O₂—The percent of oxygen in the original mixture.
- A'—The percent of methane in the exit gas.
- O₂'—The percent of oxygen in the exit gas.
- f—The fraction of the exit gas found to be CO₂.
- F—The percent of the exit gas found to be CO₂.
- x—The fraction of the original methane oxidized.
- X—The percent of the original methane oxidized.
- A''—The calculated percent of methane in the exit gas.
- O₂''—The calculated percent of oxygen in the exit gas.

¹ Z. angew. Chem., 36, 297 (1923).

² Brennstoff Chem., 5, 37 (1924).

In the following reaction, $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ if the fraction of methane oxidized is x , then the percent of methane in the gas mixture after the reaction is given by

$$A'' = \frac{100 (A - Ax)}{(A + \text{O}_2 - 2Ax)} \quad (1)$$

Likewise the percent of O_2 in the final mixture is

$$\text{O}_2'' = \frac{100 (\text{O}_2 - 2Ax)}{(A + \text{O}_2 - 2Ax)} \quad (2)$$

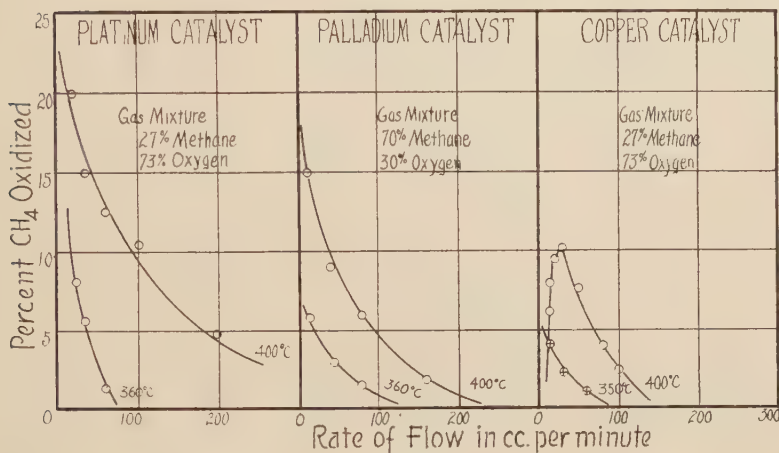


FIG. 1
Rate-Conversion Curves for the Oxidation of Methane

The percent of CO_2 in the gases after reaction is given by

$$F = \frac{Ax}{(100 - 2Ax)} \quad (3)$$

where $F = 100f$.

It is evident that the amount of methane oxidized is equal to the amount of carbon dioxide formed. For the value of x we have

$$x = \frac{100f}{A + 2Af} \quad (5)$$

Substituting the value of x from (4) in (1) and (2) we have

$$A'' = A + f(2A - 100)$$

and

$$\text{O}_2'' = \text{O}_2 + 2f(\text{O}_2 - 100)$$

The values of A'' and O_2'' given in the tables are calculated from the experimental value because f is determined experimentally. The value of O_2' was determined experimentally and the value of A' was determined by difference. The values in the tables are expressed in percentage.

TABLE I
Silver CatalystGas Mixture: (A) Methane 72.30% (O₂) Oxygen 27.70%.

Temp. °C	Rate c.c. per minute	A'	Final Analysis O ₂ '	F	100X	Calculated from F A''	O ₂ ''
360	45	83.69	10.28	6.03	7.46	74.65	20.32
360	45	72.58	27.15	0.27	0.37	72.12	27.61
360	45	72.30	27.70	0.00	0.00	72.30	27.70
360	45	72.43	27.03	0.54	0.74	72.24	27.22
360	45	72.45	26.70	0.85	1.16	72.37	26.78
250	45	98.64	1.36	0.00	0.00	72.30	27.70
250	45	73.50	26.50	0.00	0.00	72.30	27.70 ²⁵⁰
250	45	72.30	27.70	0.00	0.0	72.30	27.70
200	45	99.69	0.31	0.00	0.0	72.30	27.70
200	45	86.37	13.50	0.00	0.0	72.50	27.70
200	45	71.30	27.70	0.00	0.0	72.30	27.70
200	45	71.82	27.90	0.28	0.4	72.12	27.60

TABLE II
Copper CatalystGas Mixture: (A) Methane 69.00% (O₂) Oxygen 31.00%.

Temp. °C	Rate c.c. per Minute	Final Gas Analysis				Calculated from F	
		A'	O ₂ '	F	100X	A''	O ₂ ''
400°	15	75.12	12.60	12.28	14.29	73.67	14.10
390	12	73.75	17.65	8.60	10.65	72.26	19.12
390	25	71.25	20.45	7.80	9.79	71.96	20.24
390	45	70.94	25.80	3.36	4.57	70.28	26.40
390	75	69.75	26.32	2.93	4.00	70.11	26.93
390	200	69.12	28.90	1.98	2.76	69.75	28.20
400	200	70.12	28.00	1.88	2.63	69.71	28.40
360	15	71.98	22.05	5.97	7.73	71.27	22.70
360	15	70.63	23.25	6.12	7.90	71.32	22.55
360	200	70.00	28.95	1.05	1.49	69.40	29.50
320	15	70.86	26.90	2.24	3.11	69.85	27.90
320	200	69.21	29.45	1.34	1.89	69.50	29.16

Gas Mixture: (A) Methane 76.00%, Oxygen 24.00%

380	12	91.96	4.67	3.37	4.14	77.75	18.88
380	35	79.77	13.18	7.05	8.14	79.66	13.29
380	40	80.13	13.60	6.27	7.34	79.26	14.47
380	45	78.33	17.55	4.12	5.01	78.14	17.74
380	60	77.52	20.00	2.48	3.12	77.29	20.23
380	100	77.23	21.10	1.67	2.12	76.87	21.46
380	200	76.15	22.90	0.95	1.25	76.49	22.56

TABLE II (Continued)

Copper Catalyst

Gas Mixture: (A) Methane 27.00% (O₂) Oxygen 73.00%

Temp. °C	Rate c.c. per minute	Final Gas Analysis				Calculated from F	
		A'	O ₂ '	F	100x	A''	O ₂ ''
Gas Mixture: Methane 27.00%, Oxygen 73.00%							
400°C.	15	42.16	56.71	1.13	4.10	26.48	72.39
400	15	30.76	67.48	1.76	6.30	26.19	72.05
400	15	27.23	70.67	2.10	7.45	26.03	71.87
400	20	26.39	70.91	2.70	9.50	25.76	71.54
400	30	26.09	71.00	2.91	10.20	25.66	71.333
400	50	26.51	71.10	2.39	7.60	26.02	71.59
400	80	26.82	72.08	1.20	4.00	26.49	72.41
400	100	26.03	72.31	0.66	2.40	26.70	72.64
400	15	26.48	71.70	1.82	7.26	26.16	72.02
400	15	26.72	72.50	1.78	7.12	26.18	72.04
400	45	26.68	71.82	1.50	6.05	26.31	72.19
400	75	27.19	72.15	0.56	2.30	26.74	72.70
350	15	26.78	72.10	1.12	4.07	26.48	72.40
350	15	26.35	72.47	1.18	4.26	26.46	72.36
350	30	27.04	72.30	0.66	2.40	26.70	72.64
350	60	27.18	72.50	0.32	1.20	26.85	72.83
350	15	55.50	43.70	0.80	2.90	26.63	72.57
350	15	36.56	62.30	1.14	4.10	26.48	72.38
350	15	27.77	70.00	2.23	7.90	25.97	71.80
350	30	26.73	71.82	1.45	5.20	26.33	72.22
350	60	27.06	72.20	0.74	2.70	26.66	72.60

Gas Mixture: Methane 76.00%, Oxygen 24.00%

390	150	94.67	3.20	2.13	2.69	77.11	20.76
390	150	82.30	11.00	6.70	7.77	79.48	13.82
390	150	78.00	18.28	3.72	4.55	77.93	18.35
390	150	78.47	16.90	4.63	5.56	78.40	16.97
340	32	97.22	2.50	0.28	0.37	76.15	23.57
340	32	77.92	21.00	1.08	1.39	76.56	22.36
340	32	76.65	22.05	1.30	1.67	76.67	22.03
340	32	76.49	22.45	1.06	1.37	76.55	22.39
340	32	76.55	22.15	1.30	1.67	76.67	22.03
340	32	76.38	22.05	1.57	2.03	76.82	21.61
340	32	76.74	20.90	2.36	2.97	77.23	20.41
340	32	76.76	21.90	1.34	1.72	76.70	21.96
340	32	76.85	21.05	2.10	2.67	77.09	20.81

TABLE II (Continued)

Copper Catalyst

Gas Mixture: Methane 76.00%, Oxygen 24.00%

Temp. °C	Rate c.c. per minute	Final Gas Analysis				Calculated from F	
		A'	O ₂ '	F	100x	A''	O ₂ ''
200	50	99.46	0.54	0.00	0.00	76.00	24.00
200	50	80.63	18.85	0.52	0.68	76.27	23.21
200	50	76.53	22.95	0.52	0.68	76.27	23.21
200	50	76.16	23.30	0.54	0.70	76.28	23.18
200	50	76.14	23.40	0.46	0.60	76.24	23.30
200	50	76.05	23.25	0.70	0.90	76.36	23.00
360	45	99.31	0.28	0.41	0.54	76.21	23.31
360	45	80.00	17.40	2.60	3.25	77.35	20.05
360	45	76.78	21.30	1.92	2.35	77.00	21.08
360	45	76.57	21.80	1.63	2.08	76.85	21.52
360	45	76.58	22.10	1.32	1.69	76.69	21.39
360	45	76.38	22.04	1.38	1.77	76.72	21.90
360	45	76.35	22.30	1.35	1.73	76.70	21.95

TABLE III

Platinum Catalyst

Gas Mixture: (A) Methane 80.00% (O₂) Oxygen 20.00%

Temp. °C	Rate c.c. per minute	Final Gas Analysis				Calculated from F	
		A'	O ₂ '	F	100x	A''	O ₂ ''
365	25	86.39	3.06	10.55	11.93	86.33	3.12
365	25	87.66	0.00	12.50	12.50	87.50	0.00
365	45	87.50	0.00	12.34	12.38	87.40	0.26
365	100	87.24	0.69	12.07	12.14	87.24	0.69
365	200	87.24	0.74	11.92	12.04	87.15	0.93
330	15	87.52	0.18	12.30	12.35	87.38	0.32
330	25	87.22	0.58	12.20	12.26	87.32	0.46
330	45	86.95	0.77	12.28	12.32	87.37	0.35
330	100	86.82	0.98	11.60	11.77	86.96	1.44
330	200	86.46	2.26	11.28	11.50	86.77	1.95
250	20	82.94	12.80	4.26	4.90	82.56	13.18
250	40	81.40	16.95	1.65	2.00	80.99	17.36
250	65	81.02	18.15	0.83	1.02	80.50	18.67

Gas Mixture: (A) 78.00% Methane, (O₂) 22.00% Oxygen

300	20	84.60	2.15	13.25	13.43	85.41	1.34
300	30	84.77	2.91	12.32	12.85	84.80	2.88
300	80	84.15	5.17	10.68	11.28	83.90	5.40
300	100	83.83	5.26	10.90	11.48	84.10	5.00
300	200	85.01	3.04	11.95	12.35	87.40	3.35

TABLE III (Continued)

Platinum Catalyst

Temp. °C	Rate c.c. per minute	Final Gas Analysis				Calculated from F	
		A'	O ₂ '	F	100X	A''	O ₂ ''
Gas Mixture: (A) 27.00% Methane, (O ₂) 73.00% Oxygen							
360	25	26.40	71.30	2.30	8.15	25.94	71.76
360	35	26.13	72.30	1.57	5.65	26.29	72.14
360	60	26.72	73.00	0.38	1.40	26.88	72.74
360	200	27.00	73.00	0.00	0.00	27.00	73.00
400	20	24.78	69.10	6.12	20.20	24.18	69.70
400	35	26.25	69.30	4.45	15.10	24.95	70.60
400	60	26.29	70.10	3.61	12.50	25.34	71.05
400	100	26.39	70.60	3.01	10.50	25.64	71.38
400	200	26.86	71.80	1.34	4.80	26.38	72.28
330	25	26.40	73.20	0.40	1.47	26.82	72.78
330	25	26.56	72.55	0.59	2.16	26.73	72.68
330	25	26.84	72.55	0.61	2.20	26.72	72.67
Gas Mixture: (A) 72.00% Methane, (O ₂) 28.00 Oxygen							
400°C.	25	80.80	0.00	19.20	19.30	80.43	0.37
400	50	80.72	0.28	19.00	19.10	80.36	0.37
400	90	80.67	0.28	19.15	19.20	80.33	0.57
400	150	80.74	0.56	18.70	18.95	80.23	1.07
400	200	80.67	0.28	19.05	19.15	80.38	0.57
360	45	80.92	0.00	19.08	19.20	80.40	0.52
360	80	80.80	0.14	19.20	19.28	80.45	0.35
360	100	80.35	1.00	18.65	18.89	80.20	1.15
360	150	80.40	0.80	18.80	19.00	80.26	0.94
320	45	80.86	0.14	19.00	19.10	80.35	0.65
320	80	80.73	0.27	19.00	19.10	80.35	0.65
320	100	80.43	1.57	18.00	18.40	79.92	2.08
320	150	80.12	2.08	17.80	18.20	79.83	2.37
275	45	80.54	1.11	18.35	18.82	80.60	1.05
275	45	80.43	0.97	18.60	18.85	80.18	1.22
245	45	73.75	21.95	4.30	5.52	73.89	21.81

TABLE IV
 Palladium Catalyst

 Gas Mixture: (A) Methane 70.00% (O₂) Oxygen 20.00%

Temp.	Rate c.c. per minute	Final Gas Analysis			Calculated from F		
		A'	O ₂ '	F	100x	A''	O ₂ ''
400	15	74.92	12.28	12.80	14.56	75.13	12.07
400	15	75.12	11.58	13.30	15.00	75.33	11.27
400	40	73.24	20.40	7.21	9.00	72.89	19.90
400	80	71.33	23.60	4.57	5.98	71.83	23.60
400	160	70.00	28.40	1.44	2.00	69.42	27.98
360	15	71.05	24.69	4.55	5.72	71.74	23.91
360	45	70.00	26.75	2.19	3.00	69.12	28.67
360	80	70.31	28.60	1.09	1.55	70.44	28.47

 Gas Mixture: (A) Methane 71.50% (O₂) 28.50%

360	20	73.08	23.75	3.17	4.18	72.86	23.97
360	40	72.90	24.70	2.40	3.21	72.53	25.07
360	40	72.80	24.70	2.50	3.33	72.57	24.93
335	20	72.34	26.60	1.06	1.41	71.95	26.99
335	30	72.27	26.80	0.93	1.28	71.90	27.17
335	45	72.34	26.80	0.86	1.18	71.87	27.27

Gas Mixture: (A) Methane 27.00%, Oxygen 73.00%

400°C.	15	25.47	69.50	5.03	16.90	24.69	70.28
400	30	26.15	70.00	3.85	13.10	25.23	70.92
400	45	26.40	71.05	2.55	9.00	25.82	71.83
400	90	26.88	71.00	2.12	7.52	26.01	71.86
400	150	27.03	71.70	1.27	4.60	26.42	72.31
400	200	26.97	72.20	0.83	3.00	26.62	72.55
360	15	26.45	72.00	2.24	7.95	26.97	71.79
360	20	26.59	72.05	1.36	4.90	26.38	72.26
360	30	26.19	73.00	0.81	2.95	26.63	72.56
360	100	26.45	73.15	0.40	1.47	26.72	72.88
330	15	26.55	72.00	1.45	5.21	26.35	72.22
330	20	27.09	72.10	0.81	2.95	26.63	72.56
330	40	27.08	72.40	0.52	1.90	26.76	72.72
330	60	27.45	72.25	0.30	1.10	26.86	72.84

Discussion of Results

The results for the copper and silver catalyst are very interesting. It is evident in the case of both of these catalysts that in the early stages of the reaction oxygen is being removed from the gas stream and that this oxygen is not used in the oxidation of methane. This is indicated in Tables I and II when successive samplings are made at the same streaming rate. After the first removal of oxygen the silver catalyst shows practically zero activity throughout the temperature range studied while the copper continues to show catalytic activity. Because of this removal of oxygen in the early

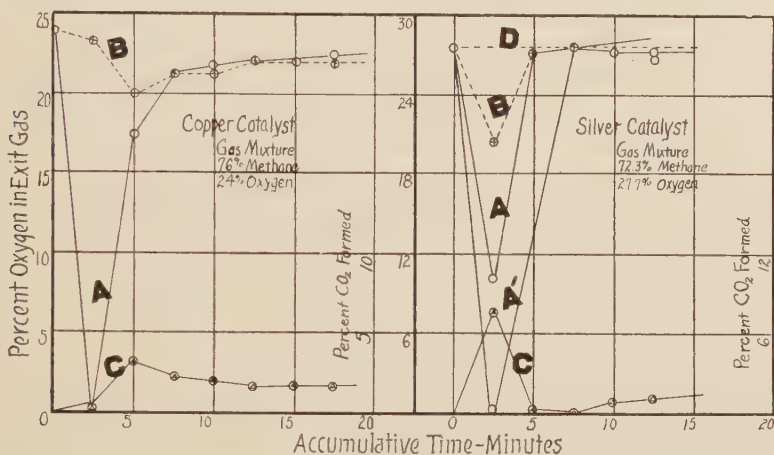


FIG. 2
Time Efficiency Curves—Oxidation of Methane

stages of reaction additional experiments were carried out. With the aid of a by pass tube around the catalyst samples were collected and analysed at $2\frac{1}{2}$ minute intervals. The results of these experiments are shown graphically in Fig. 2. In the case of the copper catalyst the temperature was 360° while in the case of the silver the curves for both 360° and 200° are given. Curves A in the case of both catalysts give the amounts of oxygen found in the gases after reaction at 360° . Curves B are for the oxygen calculated to be present from the amount of CO_2 formed and curves C are for the amounts of CO_2 found in the exit gases. Curve A' for silver is for the amount of oxygen found at 200° and Curve D gives the calculated oxygen content at 200° from the CO_2 found. There was no CO_2 found at 200° so D gives the value for the O_2 in the original gas mixture.

These experiments show quite definitely that the oxygen, which first reaches the copper and silver deposited on the silica gel, is taken up by these metals almost completely. It may be strongly adsorbed or else combined chemically to form the oxide. Since it is impossible to differentiate between these two states at present it is easier to conclude that chemical combination has taken place. In the case of copper it is probably another case where the copper must be partially oxidized before it will act as a catalyst in oxidations.

This accounts for the strange shape of the curve for the copper catalyst at 400° as shown in Fig. 1. The first measurements were made on a fresh catalyst and the first three points are those taken successively at about the same rate of flow. After reaching an equilibrium state of oxidation the catalyst behaved just as the platinum and palladium catalysts. In order to account for the rather large amount of CO_2 produced initially at 360° in the case of the silver catalyst one has to assume that the silver was acting as an oxidizing catalyst prior to being oxidized itself or else there was some adsorbed CO_2 in the catalyst. This does not seem reasonable because there was none found at 200° where adsorption should be better than at 360° . The instability of silver oxide at higher temperatures accounts for the fact that more oxygen was removed at 200° .

In the case of the platinized gel no such removal of oxygen was observed in the initial stages of reaction. The reaction seems to quickly reach an equilibrium state. Furthermore, the rate of streaming does not have much effect on the efficiency of the reaction as long as the methane is in excess. The reaction becomes measurable at about 240° . Small increases in oxygen content produce increases in the amount of oxidation. This does not hold over the total range of concentrations because an excess of oxygen does not produce complete oxidation. In fact the catalyst is less sufficient when the oxygen content is high than when it is low. For example a change from twenty to twenty-eight percent in the oxygen content of the gas sample increased the amount of methane oxidized from about twelve percent to more than nineteen percent. On the other hand an oxygen content of seventy-three percent only gives an oxidation of eight percent and the efficiency of the catalyst falls off rapidly as the rate of gas flow increases. As in other catalytic studies there is apparently a definite concentration ratio of oxygen to methane which will produce the best results. These experiments also indicate that the methane must reach the catalyst surface before it is oxidized.

In the case of the palladium catalyst the reaction does not become measurable until 330° or nearly 100° above that at which the platinized gel causes oxidation. The same general results were obtained for the palladium catalyst as for the platinum except that the palladium was less efficient at a given temperature Table IV shows that increases in the oxygen content at low concentrations of oxygen causes more reaction while oxygen in excess leads to lessened reaction. The difference in the efficiency between the platinum and palladium may be due to the fact that the platinized gel is a slightly better adsorbent of oxygen. This is shown in the adsorption studies¹ on these gels.

Summary

1. With the exception of the silver catalyst the metallized silica gels have been shown to act catalytically in the oxidation of methane. They promote the complete oxidation of methane, yielding carbon dioxide and water. No partial oxidation products were found.

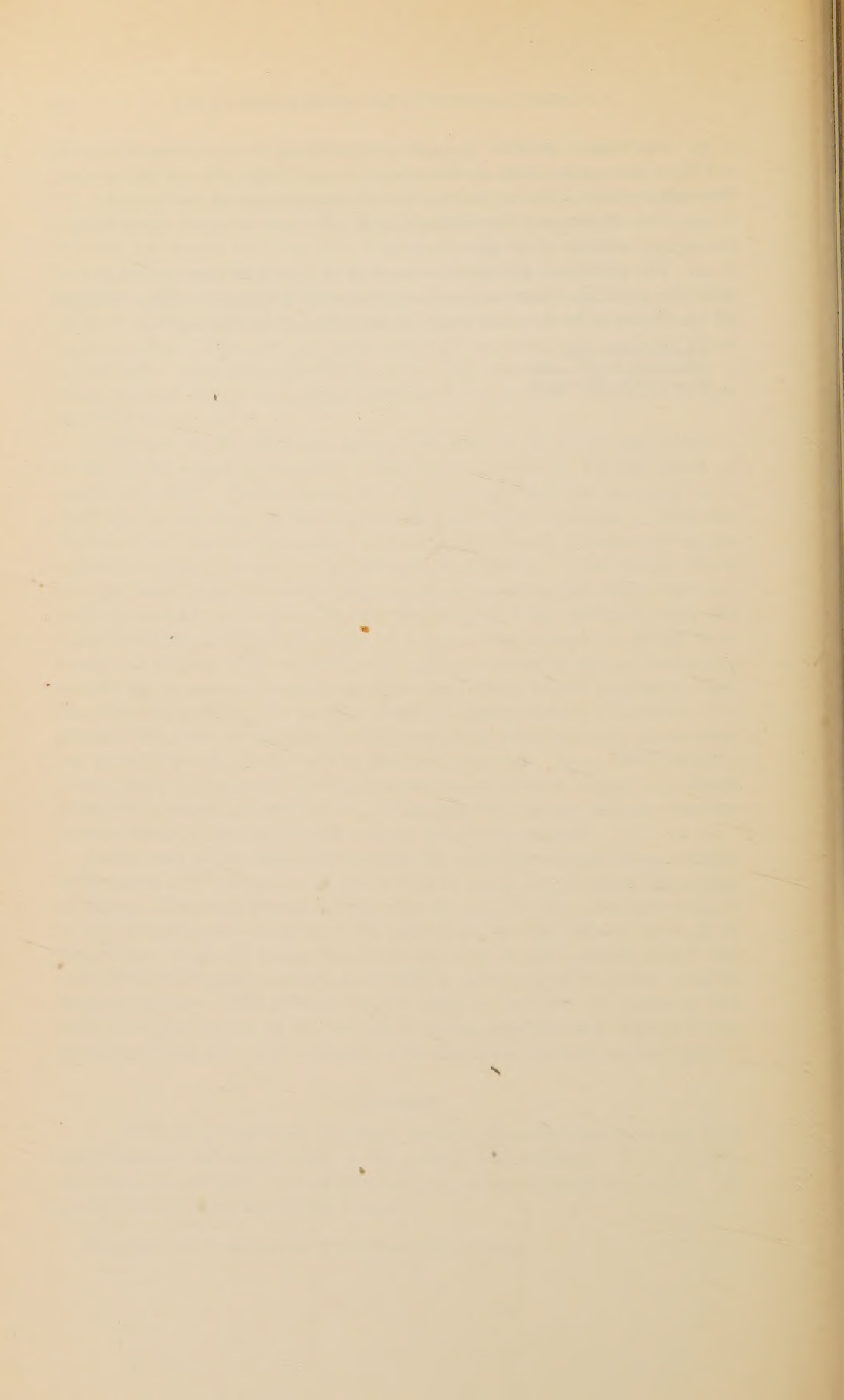
¹ Reyerson and Swearingen: J. Phys. Chem., 31, 88 (1927).

2. The copper catalyst is apparently oxidized to a considerable extent and then the copper oxide or the copper, copper oxide acts as the catalyst. The copper catalyst starts the reaction at a temperature as low as 200° .

3. The efficiency of the platinum and palladium catalysts depends upon the oxygen content of the gas mixture.

4. The platinized gel initiates reaction at a temperature as low as 240° while the palladium does not become active until about 330° . The platinized gel was found to be the most active of the catalysts in this reaction.

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VITA

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